

## 5.5. SPECIAL PROJECTS

### 5.5.1. METHYL HALIDE EMISSIONS FROM TOMATO PLANTS

#### Fieldwork

The atmospheric budgets of most natural halocarbons are poorly defined. For both methyl bromide ( $\text{CH}_3\text{Br}$ ) and methyl chloride ( $\text{CH}_3\text{Cl}$ ), best estimates of the known sinks outweigh best estimates of the known sources by 30-50% [Kurylo *et al.*, 1999]. Although plant production of natural halocarbons has not been studied extensively, there is considerable new evidence that plants are involved in the cycling of these compounds. Previous studies have primarily involved the use of a flux chamber, which does not isolate the plant from the soil and potentially stresses the plant [e.g., Gan *et al.*, 1998; Redeker *et al.*, 2000; Rhew *et al.*, 2000, 2001]. Soils are potentially problematic because they have been observed to remove  $\text{CH}_3\text{Br}$  from the atmosphere [e.g., Varner *et al.*, 1999].

The HATS group conducted an experiment in a hydroponic greenhouse in Northern California (McKinleyville) over a 2-wk period in July 2001. The greenhouse was covered with double-layered polyethylene and housed about 400 tomato plants (*Lycopersicon esculentum*). The plants were grown in bags of inert support material (Pearlite) without soil and were flushed with an aqueous nutrient mixture at frequent intervals throughout the day. During each experiment, the greenhouse was sealed, and halocarbon concentrations were measured in the greenhouse atmosphere with a GC-MSD located at the site. Sampling lines were placed in the center and at one end of the greenhouse. Fans were used to keep the greenhouse atmosphere well mixed. No concentration differences were observed between the two sampling locations. Experiments were started in the late afternoon/early evening and were run until the air temperature in the greenhouse exceeded about  $35^\circ\text{C}$ , usually about noon the following day. Eight experiments were run in total, and each experiment lasted 16-20 hours. The standard nutrient mixture was used first for two control experiments (C-1 and C-2). This nutrient mixture contained no significant halide concentrations. A solution containing about 5 ppm  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{I}^-$  was added in line with the nutrient mixture during the third, fourth, and fifth experiments (H5-1, H5-2, and H5-3). During the final three experiments (H20-1, H20-2, and H20-3), a solution of about 20 ppm  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{I}^-$  was added in line with the nutrient mixture. These halide solutions were added continuously over the course of several days, not just during the experiments themselves.

#### Results and Discussion

During C-1 and C-2, no production of  $\text{CH}_3\text{Br}$  (Figure 5.36a) or  $\text{CH}_3\text{Cl}$  was observed, but methyl iodide ( $\text{CH}_3\text{I}$ ) (Figure 5.36b) increased by a factor of about 5 by the end of the experiments. Production was also observed for several other halogenated compounds, including bromochloromethane ( $\text{CH}_2\text{BrCl}$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), and bromoform ( $\text{CHBr}_3$ ) (Figure 5.36c). In general,

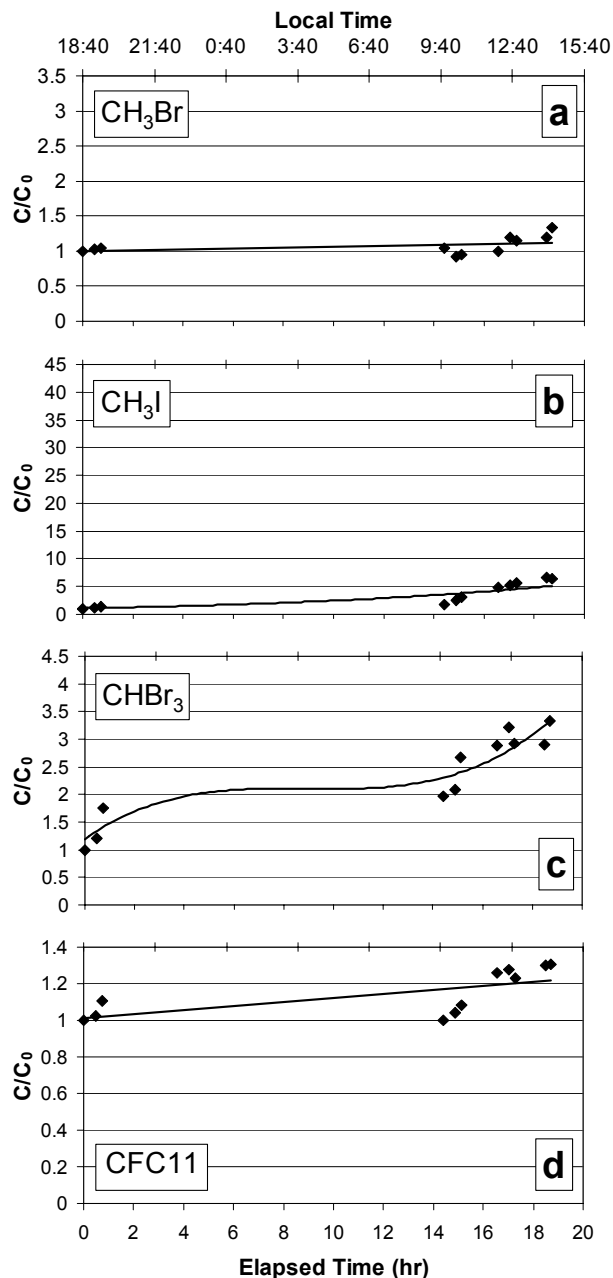


Fig. 5.36. Concentration changes of (a)  $\text{CH}_3\text{Br}$ , (b)  $\text{CH}_3\text{I}$ , (c)  $\text{CHBr}_3$ , and (d) CFC-11, during a greenhouse experiment, plotted as a function of time. All concentrations were normalized to the corresponding initial concentration ( $C/C_0$ ). During this experiment, no halide ions were added to the nutrient mixture.

anthropogenic compounds, such as CFC-11 (Figure 5.36d), CFC-113, and halon-1211, remained relatively constant over the course of the study, suggesting that large-scale contamination from materials in the greenhouse or from the greenhouse itself was unlikely.

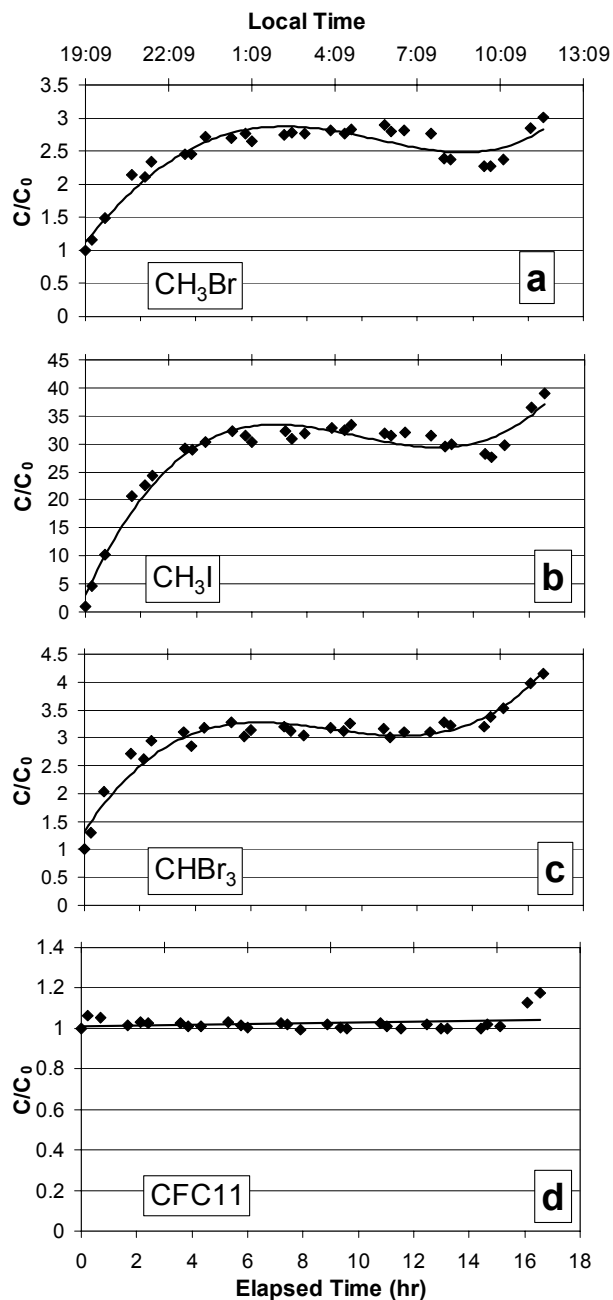


Fig. 5.37. Concentration changes of (a) CH<sub>3</sub>Br, (b) CH<sub>3</sub>I, (c) CHBr<sub>3</sub>, and (d) CFC-11, during a greenhouse experiment, plotted as a function of time. All concentrations were normalized to the corresponding initial concentration ( $C/C_0$ ). During this experiment, a solution containing about 20 ppm Br<sup>-</sup>, Cl<sup>-</sup>, and I<sup>-</sup> flushed the plants with the nutrient mixture.

The addition of the halide solution affected the production rates of only CH<sub>3</sub>Br and CH<sub>3</sub>I (Figure 5.37a,b). During experiments H20-1, H20-2, and H20-3, CH<sub>3</sub>Br increased by nearly a factor of 3. Production of CH<sub>3</sub>I increased by a factor of about 35 during these experiments, almost an order of magnitude more than with the standard nutrient mixture alone. Production for other halogenated compounds, such as CHBr<sub>3</sub> (Figure 5.37c) and CHBr<sub>2</sub>Cl, did not change noticeably between experiments run with and without the halide solution.

Similar results were observed for the H5 experiments. Only CH<sub>3</sub>Br and CH<sub>3</sub>I production differed from the other experiments. The production for those two compounds increased with each experiment. Production during H5-3 approached the values that were observed during the H20 experiments. This suggests that production of CH<sub>3</sub>Br and CH<sub>3</sub>I by tomato plants is a function of halide concentration. More studies are necessary to determine if these observations are reproducible for these and other plants.

Although tomato plants were chosen for little other reason than opportunity, this study suggests that many plants could emit significant amounts of organic halogens to the atmosphere. It also supports propositions from other investigators that there is a relationship between halide concentration in the soil and organic halogen production by plants [e.g., Redeker *et al.*, 2000; Rhew *et al.*, 2000]. This preliminary study has raised many questions. One question concerns the production of polybrominated compounds when no halides were added, whereas CH<sub>3</sub>Br concentrations remained constant. It is also unknown why the production of CH<sub>3</sub>Br and CH<sub>3</sub>I increased with the addition of the halide solution while that of other halocarbons did not. The potential variability of production rates as a function of plant growth stage was also not addressed in this study. Further studies of these and other plants will be necessary before these questions can be adequately addressed.